Reaction of Diphenylketen with *N*-Alkyl Nitrones

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Summary Diphenylketen reacts with the *N*-alkyl nitrones (**3**) to form β-lactams (**4**) and oxazolones (**5**).

THE reaction of nitrones with cumulenes has been shown[1] to proceed with a rearrangement, leading to products other than the expected 1,3-dipolar adducts. Our own work[2] with the reaction of diaryl nitrones with ketens has shown that the normal reaction pathway for these compounds involves initial formation of a zwitterion (**1**) followed by sigmatropic rearrangement to (**2**), one or more further steps leading to the observed products. We now report studies on the reaction of ketens with *N*-alkyl nitrones for which no similar reaction path is available.

Diphenylketen reacted with the *N*-methyl nitrone (**3a**) in benzene to give two products. One, $C_{28}H_{21}NO$, m.p. 201°, was identified as the β-lactam (**4**) by the i.r. spectrum and comparison with a synthetic specimen obtained by addition of diphenylketen to *N*-methylfluorenoneimine. The product presumably arises by deoxygenation of (**3a**) to the imine, which subsequently reacts with more diphenylketen. The second product, $C_{28}H_{21}NO_2$, m.p. 145°, has a molecular formula corresponding to a 1:1 adduct of keten and nitrone, and is assigned the structure (**5**) rather than that of the expected 1,3-dipolar adduct (**6**) on the basis of spectroscopic data and degradative evidence. Reduction of the adduct with lithium aluminium hydride gave a dihydro-derivative (**7**), m.p. 177°, containing a methyl group, a methine group, and a hydroxy-group, which decomposed during chromatography on silica gel to give fluorenone in almost quantitative yield. Treatment of the adduct with benzylamine in methanol gave, amongst other products, a compound with properties similar to those of 2-methylamino-2,2-diphenylacetic acid, which was reduced by lithium aluminium hydride to the amino-alcohol (**8**) and identified by comparison with a synthetic specimen.

On boiling a solution of the adduct (**5**) in benzene, a dark green colour developed, whereas boiling the adduct in benzene in the presence of dimethyl acetylenedicarboxylate leads to formation of a compound $C_{33}H_{27}NO_4$, m.p. 196°, with spectroscopic properties consistent with the structure (**9**). We believe the green colour is due to formation of a stable ylide (**10**) formed by loss of carbon dioxide from (**5**).

Reaction of diphenylketen with the *N*-ethyl and *N*-isopropyl nitrones (**3b,c**) gave products similar to (**4**) and (**5**). The mechanism of formation of (**5**) is not clear, although it can be rationalised in terms of the mechanism suggested by Cum[1] for the reaction of allenes and nitrones.

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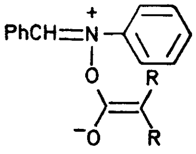
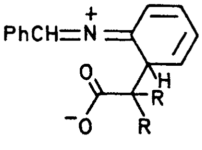
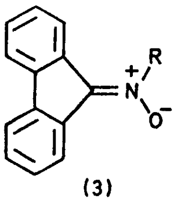


(1)

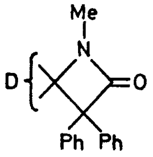


(2)



(3)

(a) R = Me
(b) R = Et
(c) R = Pr^i



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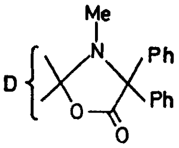
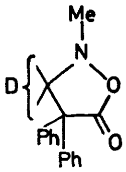
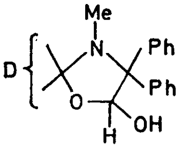


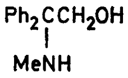
(5)



(6)

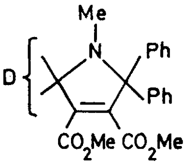


(7)

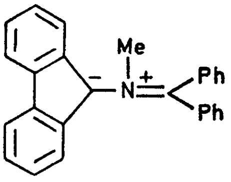


$$\begin{array}{l}Ph_2\underset{\displaystyle MeNH}{\underset{|}{C}}CH_2OH\end{array}$$

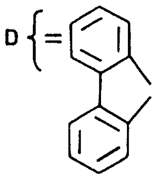
(8)



(9)



(10)



(11)

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[1] M. C. Aversa, G. Cum, and N. Uccella, *Chem. Comm.*, 1971, 156; M. C. Aversa, G. Cum, G. Stagno d'Alcontres, and N. Uccella, *J.C.S. Perkin I*, 1972, 222.

[2] R. N. Pratt, D. P. Stokes, G. A. Taylor, and P. C. Brookes, *J. Chem. Soc.* (*C*), 1968, 2086; D. P. Stokes and G. A. Taylor, *ibid.*, 1971, 2334.